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# SYNTHESIS OF PIGMENTS BASED ON PEROVSKITE

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The results of synthesis of pigments based on perovskite ($CaTiO_3$) are presented. Differential thermal and x-ray phase analysis methods are used to study the processes occurring in heat treatment and to determine the phase composition of the yellow pigment based on nickel titanate. The expediency of producing this pigment by the precipitation method is demonstrated. The color characteristics of the pigment and the area of application are indicated.

Refractory pigments for ceramic paints are produced on the basis of crystal structures of spinels, garnets, zircon, mullite, etc. Considerable recent attention has been focused on the crystal structure of perovskite ($CaTiO_3$) in the context of synthesis of pigments. Perovskite is characterized by a cubic structure with a unit cell parameter equal to 3.84 E ($a'$), which is the perfect structure. In fact, perovskite has rhombic syngony with the following parameters:

$$a \quad 5.37\ \text{E} \sim \sqrt{2a'};$$
$$b \quad 7.63\ \text{E} \sim \sqrt{2a'};$$
$$c \quad 5.43\ \text{E} \sim \sqrt{2a'}.$$

The cubic cell has a titanium atom in its center, a calcium atom in the vertexes, and an oxygen atom on the faces. Such a structure is typical of compounds with the general formula of $ABX_3$ (A — $Ca^{2+}$, $Sr^{2+}$, $Cd^{2+}$, $B^{2+}$, $Ni^{2+}$, $Co^{2+}$; B — $Ti^{4+}$, $Zr^{4+}$, $Sn^{4+}$, etc.; X — $O^{2-}$). The sum of the A and B valences has to be equal to 6 [1].

The titanium dioxide that forms a part of the perovskite structure exists in three modifications: anatase, brookite, and rutile. Anatase changes to rutile at the temperature of 915°C, and brookite at 650°C [2]. Rutile has a tetrahedral crystal structure and is yellow in color. In the course of heat treatment of $TiO_2$ with coloring oxides (CoO and NiO), titanates with the structure of perovskite are formed. The crystal structure of perovskite contains two types of cations and one anion in the ratio of $Ca^{2+} : Ti^{4+} : O^{2-}$ equal to 1 : 1 : 3. A considerable number of mixtures and solid solutions satisfy this stoichiometric criterion.

In the present study, the $Ca^{2+}$ ions in perovskite were partly or completely replaced with $Ni^{2+}$ and $Co^{2+}$ ions. Sodium carbonate $Na_2CO_3$ was used as a mineralizer in the amount of 5% of the total weight of the mixture. Finely pulverized powders of the initial components were carefully mixed and heat-treated at 950 – 1050 – 1100°C with 1-h holding.

The samples containing NiO and $TiO_2$ acquired a more saturated shade of yellow with an increase in the amount of nickel oxide and the temperature. The color of the samples based on CoO and $TiO_2$ with an increase in the CoO concentration and temperature varied from gray to greenish-blue. The intensification of the yellow color is due to the shift of the nickel absorption band toward the red and orange regions of the spectrum [3] under the effect of titanium ions, which have a high charge and small ionic radius. The amount of NiO in the composition of perovskite was 0.2 – 1.0 mole, and the content of CaO in this case decreased accordingly. The same method was used in replacing calcium oxide with cobalt oxide:

$$(1-x)\text{CaO} \cdot x\text{CoO} \cdot \text{TiO}_2,$$

where $x = 0.2 - 1.0$CoO, NiO.

The obtained samples were investigated employing differential thermal analysis. The DTA curves of the synthe-

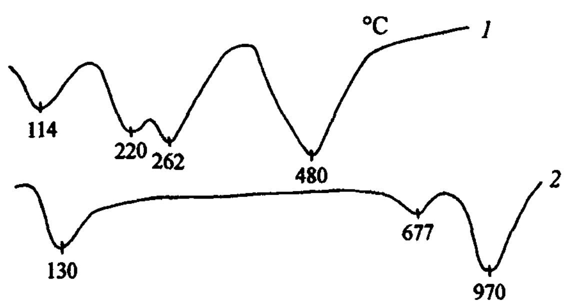


**Fig. 1.** DTA curves of synthesized pigments. *1*) NiO – $TiO_2$; *2*) CaO – CoO – $TiO_2$.

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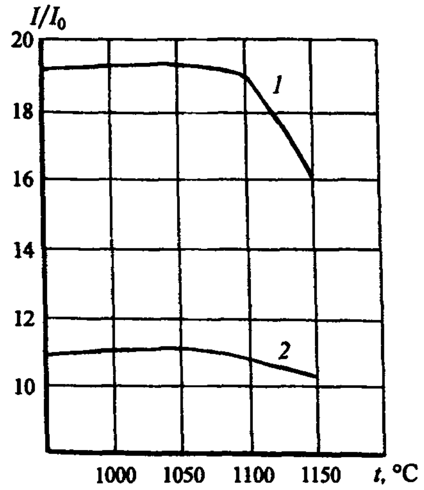


**Fig. 2.** Temperature dependence of the intensity of rutile diffraction maximum. *1*) $d = 3.25$ E, *2*) $d = 1.27$ E.

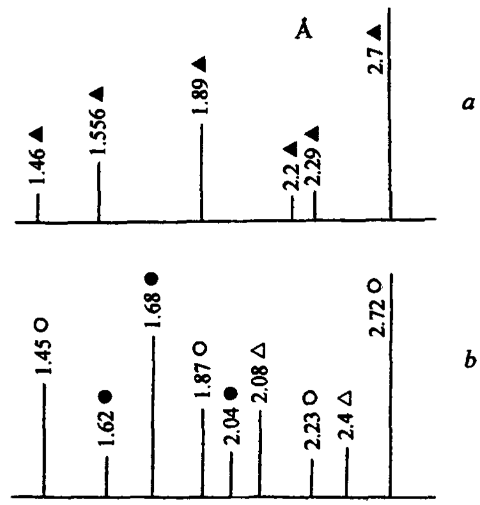


**Fig. 3.** X-ray diffraction patterns of $CaTiO_3$ (*a*) and NiO – $TiO_2$ at the temperature of 1150°C (*b* ). O) $NiTiO_3$; ●) rutile; △) NiO; ▲) $CaTiO_3$.

sized pigments are shown in Fig. 1. The curves exhibit endothermic and exothermic effects of solid-phase reactions: dehydration, decomposition of carbonates, and polymorphic transformations.

The samples were also investagated using x-ray phase analysis (DRON-2 unit). The analysis of the x-ray patterns of the fired mixtures of nickel and titanium oxides indicated that with an increase in the temperature from 1100 to 1150°C, the intensity of the rutile peaks significantly decreases (Fig. 2).

The x-ray phase analysis of the process of nickel titanate formation established that with an increase in temperature up to 1150°C, $NiTiO_3$ is formed. The x-ray patterns reveal a gradual decrease in the reflections typical of rutile and nickel oxide and the appearance of perovskite reflections (2.7, 1.87, 1.6 E). This is visible in the x-ray diffraction pattern of the initial perovskite and nickel titanate (Fig. 3). However, the reflections of the initial oxides are still partly preserved. Regarding the formation of $CoTiO_3$, it should be noted that within the above mentioned limits of heat treatment, the x-ray patterns mainly exhibit the reflections belonging to the individual oxides of the synthesized cobalt-bearing perovskite.

For comparison of the technological properties, the pigments were also synthesized by the precipitation method [4], using a 1-M solution of $NiSO_4 \cdot 7H_2O$ salt and introducing crystalline $TiO_2$. A 1-M solution of NaOH was used as a precipitator. The quantity required for complete precipitation of $Ni(OH)_2$ was determined from the pH-metric titration curve on an EV-74 universal ionometer.

The x-ray phase and differential thermal analysis established that in precipitation, not only $Bi(OH)_2$ is formed but nickel titanate as well, due to a partial reaction of the initial components. Since $TiO_2$ was added to the solution in the powdered form, only nickel hydroxide was precipitated on addition of the alkali, but in aging of the precipitate, the $TiO_2$ reacted to it and produced nickel titanate. Apparently in this case, the following reaction took place:

$$Ni(OH)_2 + TiO_2 \xrightarrow{\text{High-alkaline medium}} NiTiO_3 + H_2O.$$

The release of water is observed on the thermograms, and the $NiTiO_3$ reflections are registered in the x-ray pattern. After drying, the obtained precipitate was introduced in a glaze composition in grinding without preliminary firing. The color of the glaze coating was similar to the one obtained in using pigments synthesized by the powder method. The obtained yellow pigment of perovskite structure has a brightness of 54%, and color purity of 66%.

Thus, the results of the experiments support the expediency of using the precipitation method for production of yellow pigments, since this method makes it possible to exclude such power-consuming operations as grinding and preliminary firing of synthesized pigment. The obtained pigment can be recommended for glaze coloring in production of ceramic tiles.

## REFERENCES


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